



# Non-Polluting Composites Repair and Remanufacturing for Military Applications: Co-Injection Resin Transfer Molding

by Bruce K. Fink and John W. Gillespie Jr.

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# **Army Research Laboratory**

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## **Non-Polluting Composites Repair and Remanufacturing for Military Applications: Co-Injection Resin Transfer Molding**

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## Abstract

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Vacuum-assisted resin transfer molding (VARTM) processes have been proven to be cost-effective manufacturing techniques for large composite structures. However, their use has been limited to single resin systems. A large variety of composite structures requires multiple resins to serve different purposes while being integrated into a single structure. Significant environmental cost savings are possible by replacing currently practiced sequential repair and manufacturing techniques with reduced-step co-cure processes enabled by the co-injection resin transfer molding (CIRTM) variant of the VARTM process. The CIRTM process was investigated to manufacture two dual-layered structures commonly required in Department of Defense (DOD) structures. The first consists of a vinyl-ester layer for structural integrity and a phenolic layer for flammability, smoke, and toxicity (FST) protection. The second consists of structural epoxy with a polyurethane layer for improved damage tolerance. In each case, the two resins are simultaneously injected into a mold filled with a stationary fiber bed and co-cured. Resin separation is maintained by a 1-mil-thick polysulfone film sandwiched between two layers of 6.5-mil-thick adhesive. Various tests have been performed to demonstrate mechanical, thermal, and rate-dependent performance of the improved structures.

## **Acknowledgments**

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# 1. Introduction

Vacuum-assisted resin transfer molding (VARTM) and co-injection resin transfer molding (CIRTM) are manufacturing techniques and repair procedures that allow for the repair of more complex polymer-matrix composite (PMC) components and provide the required localized temperature and pressure needed for repair without the use of an autoclave. VARTM starts with placement of a continuous-fiber reinforcement in a closed mold. Resin injected while the mold is under vacuum flows through the reinforcement and fills the mold. VARTM has proven to be very cost effective in the manufacture of large composite parts, but it has been used primarily with single-resin systems. CIRTM expands VARTM capabilities by enabling the injection of multiple resin systems into a single fiber lay-up in a single mold/vacuum-bag procedure. Several techniques have been developed that define procedures for maintaining and controlling the separation of flow between multiple resins through the thickness of the part. By using a single-step co-cure process that injects multiple-resin systems, CIRTM offers the potential to satisfy multifunctional requirements, reduce costs, and increase quality, performance, and durability. CIRTM eliminates the need for secondary bonding operations. Both resin transfer molding (RTM) methods are completely closed systems that trap volatile organic compounds (VOCs), reduce the need for solvents, and result in less scrap than other processes. VARTM and CIRTM provide the means for getting the composite material into the mold/vacuum bag, where they may be cured via E-beam or induction methods.

The need certainly exists for processing technologies that simplify the integration of complex designs and thereby simplify repair and reduce reliance on bonding agents for multilayered multifunctional structures. Existing manufacturing technologies cannot fabricate these integrated structures in a clean and simple process. For example, polymer-composite-based integral armor requires an extensively layered and bonded structure. The current multistep process involves multiple vacuum bagging, tooling, and adhesive-bonding operations, leading to multiplicity in environmentally hazardous emissions, scrap production, and consumable use and waste (e.g., vacuum-bag material waste). If put into production, the composite armored vehicle (CAV) platform vehicle would use more than one million pounds of glass/thermoset resin composites

manufactured in more than three million separate composite structure processing operations per year. For complex structures like this, repair operations would require (1) removing material by media blasting; (2) applying cutting media, cleaning agents, and solvent wiping; (3) building multiple layers; (4) rebonding multiple interfaces with adhesives; and (5) autoclaving the repair in multiple steps.

VARTM processes have been proven to be cost-effective manufacturing techniques for large composite structures. However, their use has been limited to single resin systems. A large variety of composite structures requires multiple resins to serve different purposes while being integrated into a single structure. Significant environmental cost savings are possible by replacing currently practiced sequential repair and manufacturing techniques with reduced-step co-cure processes enabled by the CIRTM variant of the VARTM process [1]. CIRTM enables the user to manufacture multilayer hybrid composite parts in a single processing step. Key issues that currently limit the use of this new technology for environmentally friendly repair and remanufacturing need to be addressed. The CIRTM process was investigated to manufacture two dual-layered structures commonly required in Department of Defense (DOD) structures. The first consists of a vinyl-ester layer for structural integrity and a phenolic layer for flammability, smoke, and toxicity (FST) protection. The second consists of structural epoxy with a polyurethane layer for improved damage tolerance. In each case, the two resins are simultaneously injected into a mold filled with a stationary fiber bed and co-cured. Resin separation is maintained by a 1-mil-thick polysulfone film sandwiched between two layers of 6.5-mil-thick adhesive. Differential scanning calorimetry (DSC) is used to select the optimum cure cycle for all of the materials. Mechanical testing is used to evaluate the performance of the interphase formed between dissimilar materials. Short beam shear (SBS) is used to evaluate the overall quality of the part produced. Specialty testing is also performed to demonstrate the salient features of each material system including flammability testing and low-velocity impact testing.

Mechanical characterization of the CIRTM parts suggests that the choice of materials is critical to the CIRTM process. A number of alternatives were evaluated. Chemical

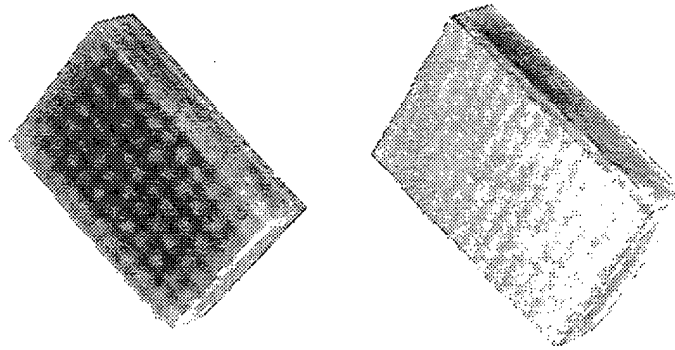
compatibility of the base composite resins with the film adhesive is critical for interphase quality. Results showed that, with proper selection of constituent materials and cure cycles, the interlaminar shear strength provided by CIRTM is enhanced relative to the weakest resin in the specimen. In all CIRTM specimens, shear failure occurred within the phenolic. For the Mode I fracture toughness testing, failure of the co-injected samples was observed to be cohesive, while failure of the secondary bonded samples was adhesive failure between the epoxy adhesive and the phenolic composite. During Mode I crack propagation, multiple delamination planes formed in the phenolic laminate, which is a reflection of the higher toughness offered by the CIRTM interphase. Results of both interlaminar shear and Mode I fracture toughness for the CIRTM were comparable to or exceeded the phenolic baseline. The fire performance characteristics of the CIRTM laminates offered superior protection in terms of peak rate of heat release and time to ignition. Further improvements to the FST performance are possible through optimization of the relative thicknesses of each resin layer.

Table 1 shows the various resins system and fiber preforms that have been successfully co-injected.

**Table 1. Co-Injected Fiber Preforms and Resin Combinations**

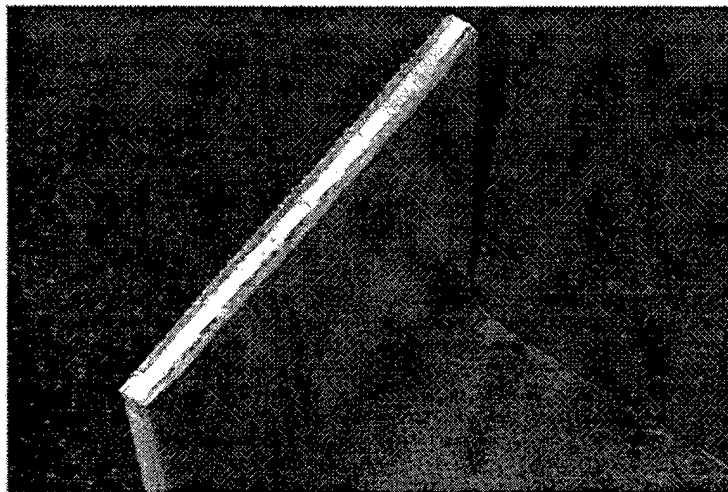
Fiber Preforms	Resin Combinations
Carbon	Epoxy/urethane
Glass	Epoxy/vinyl ester
	Epoxy/phenolic
	Vinyl ester/phenolic
	Vinyl ester/urethane
	Phenolic/urethane

Various end item articles and configurations, such as flat plates, angle bends, and integral armor components, have also been fabricated. Examples of these articles are shown in Figures 1-4.



*Note: This component has a structural vinyl-ester resin on one side and a fire-protective phenolic resin on the other.*

**Figure 1. Co-Injected Dual-Resin Component.**

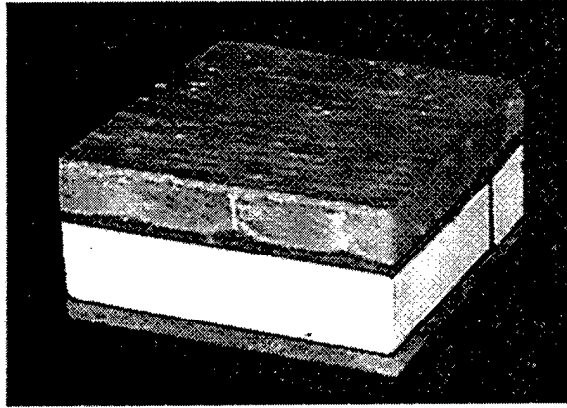


*Note: This part demonstrates scaleup of the process to large angular components.*

**Figure 2. Co-Injected Angle Section With Balsa Core.**

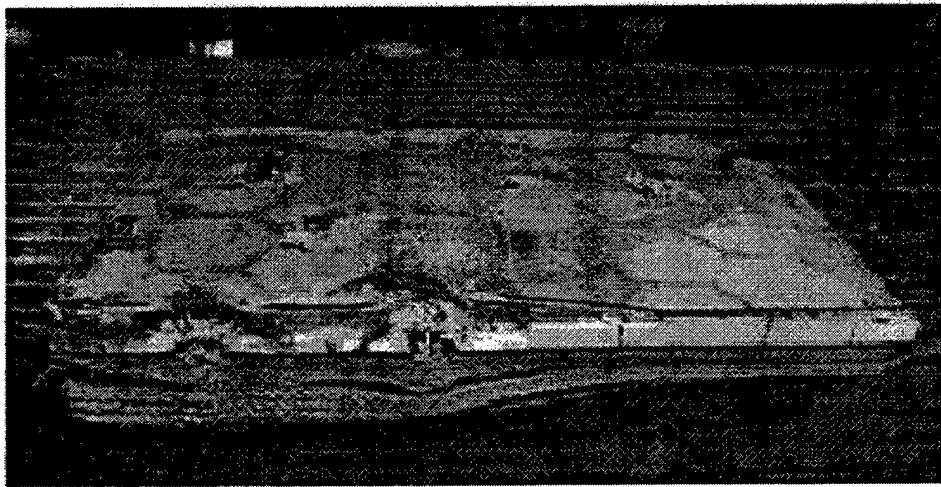
The benefits of low-cost VARTM processing are being explored for composite repair procedures. VARTM processing offers the advantage of room-temperature storage of materials, long to infinite storage life, and room/low-temperature-cure resin systems. The CIRTM process is now being evaluated for repair of multifunctional composites and cored composite structures. CIRTM offers the ability to repair these multifunctional hybrid composites in a single step,





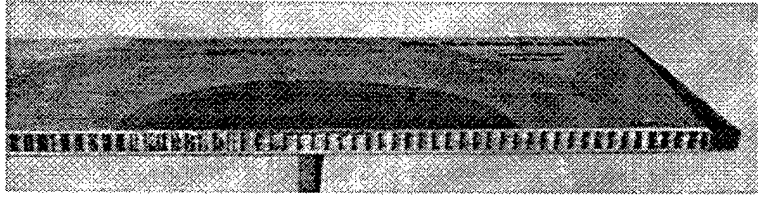
*Note: This component demonstrates the injection of three different resins (structural, fire-protective, and energy-dissipative resins) into a complex multifunctional component. This example also demonstrates the through-thickness reinforcement enabled by the CIRTM process.*

**Figure 3. Co-Injected Integral Armor.**



**Figure 4. Example of Improved Ballistic Protection Through Co-Injection and Stitching.**

restoring the structure to its original state. An example of a VARTM repair to a honeycomb structure is shown in Figure 5.



**Figure 5. Example of VARTM Repair of Honeycomb Core Structure.**

The application of CIRTM to Navy structures such as the Advanced Enclosed Mast/Sensor (AEM/S) System, currently on the USS Radford and slated for production, is dependent on the identification of compatible resin systems that meet the needs of the Navy. The following sections outline processing and testing results for vinyl-ester/phenolic and urethane/epoxy composites of interest to the Navy and of general value to a wide variety of DOD requirements. More detail is provided in Gillio et al. [2] and McKnight et al. [3, 4].

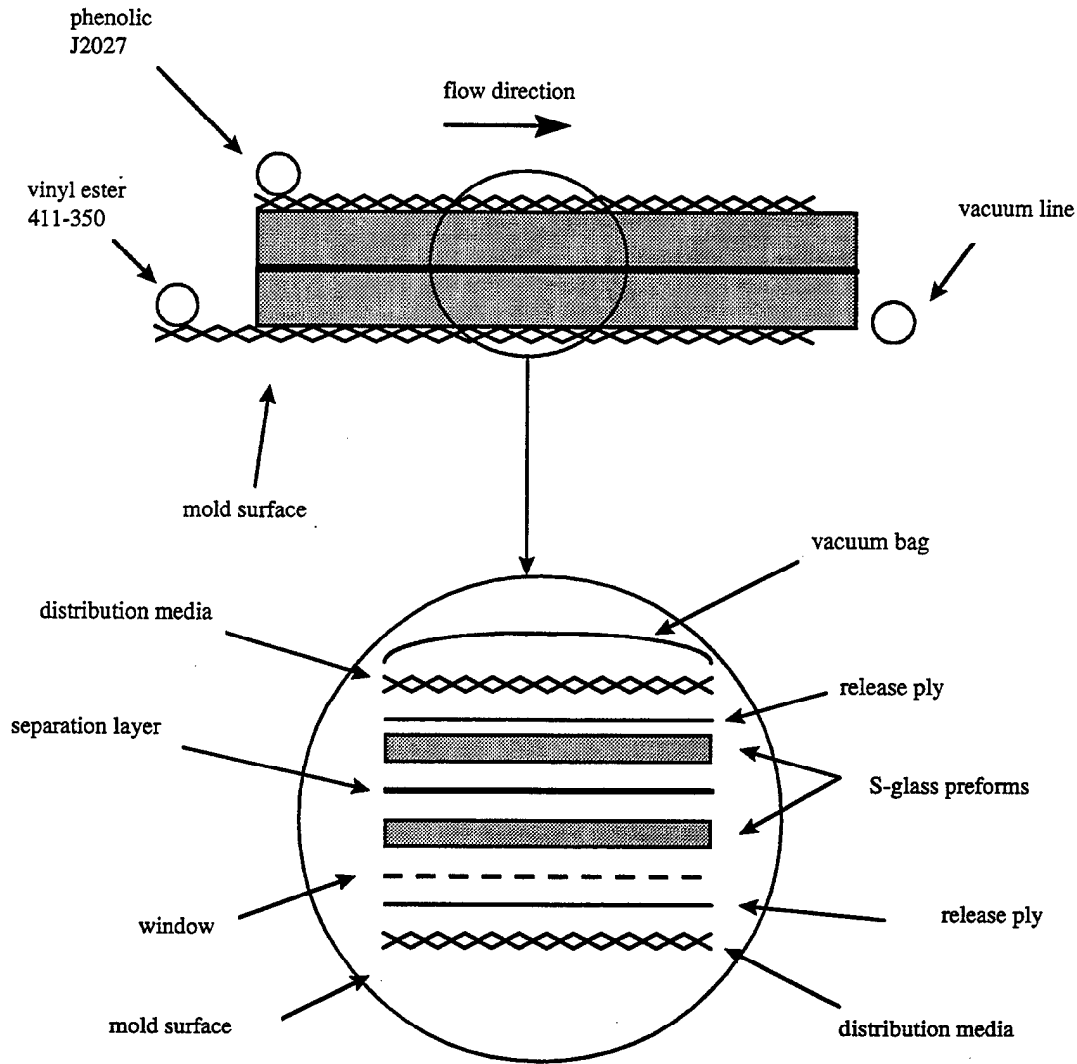
## **2. Processing and Properties of CIRTM-Processed Vinyl-Ester/Phenolic Composites**

**2.1 Background and Motivation.** Composite materials have a number of advantages over traditional materials. Some of these advantages are light weight, high stiffness-to-weight ratio, improved signature management, and resistance to corrosion. In most cases, one material cannot serve all of these functions, but various materials can be easily layered to serve multiple tasks while being integrated in a single structure. For example, vinyl esters are low-cost resins that offer good mechanical properties, room-temperature cure, and reliable processing. However, they are extremely flammable and produce toxic smoke upon combustion, limiting their use in applications where material flammability is a concern. Phenolic resins offer low cost but poor mechanical properties due to the evolution of water during cure. However, they offer outstanding FST protection [5]. Using CIRTM, a single structure can be manufactured with a thick layer of vinyl ester to take advantage of its mechanical properties and a thin layer of phenolic to act as an FST barrier.

Pike, McArthur, and Schade [6] have shown that VARTM processes are cost-effective methods for the manufacture of large structures. CIRTM takes advantage of these methods and improves them by enabling manufacture of multilayer structures in a single-processing step. Prior to CIRTM, the layers would typically be manufactured individually and then bonded together. This approach requires multiple steps, including surface pretreatments and adhesive bonding, which can introduce additional defects into the part. CIRTM eliminates all of these additional steps, lowers costs, and can improve quality and performance of the part due to the co-cure feature of the process. The fundamentals of CIRTM are investigated in detail by Gillio et al. [7, 8]. In this study, the CIRTM process is described and used to fabricate glass-reinforced vinyl-ester/phenolic hybrid composites. Parts are subjected to a variety of tests to characterize mechanical properties and durability of the interphase formed during co-injection and co-cure.

**2.2 Manufacturing Procedure.** In the vast majority of structural applications, the vinyl-ester layer would be considerably thicker than the phenolic layer. However, in this research the co-injected preforms were of equal thickness. This was done because the mechanical tests performed to evaluate the interphase properties require that the interface between the dissimilar materials be located at the geometric midplane. Additionally, the Mode I interlaminar fracture specimens (double cantilever beam [DCB]) and the wedge test require that the precrack be placed at the midthickness between two cantilever beams of comparable stiffness. Therefore, under the assumption that the modulus is a fiber-dominated property, the panels were manufactured with the same fiber reinforcement throughout the thickness. Sublaminates infiltrated with each type of resin were assumed to have the same modulus.

Figure 6 shows the experimental setup used to manufacture the co-injected specimens. Seven layers of S2-glass twill-weave 18-oz/yd<sup>2</sup> fabric were used for the phenolic and vinyl-ester preforms. The vinyl ester used in this study was Dow Derakane 411-350, which is a room-temperature vinyl ester with a gel time of approximately 30 min. The phenolic used was J2027/L, which is manufactured by British Petroleum and cures at approximately 140°F. An impermeable separation layer was used between them to demonstrate the feasibility of this



**Figure 6. Experimental Setup Used to Manufacture Co-Injected Specimens.**

method for large composite structures. The need for an impermeable separation layer was investigated by Gillio et al. [9]. The setup used in this study is typical of the Seemann Composites Resin Infusion Molding Process (SCRIMP) [10]. The distribution medium placed on each side of the preforms is a high-permeability material that helps to carry the flow along the length and width of the part while the resin flows through the thickness of the preform. The distribution medium drastically reduces fill times and enables thick-section parts to be impregnated under vacuum only. The resins were simultaneously injected from the two injection

locations shown in the figure. Once the part was infused and the resin had cured, the distribution medium was removed.

The impermeable separation layer was formed of a polysulfone film sandwiched between two layers of epoxy-based adhesive. This solution exploits the diffusion-enhanced adhesion (DEA) [11–13] mechanisms, whereby epoxy and the amine curing agent diffuse and react in the polysulfone barrier layer. A 1-mil-thick polysulfone film was selected to go into solution quickly with the epoxy and to toughen the interphase during cure. Additionally, the phenolic is co-cured with the compatible epoxy. The approach provides a toughened co-cured interphase between materials that would not otherwise be compatible.

The manufacturing took place in the following steps. First, the mold surface, a flat steel plate, was cleaned and mold release was applied to it. Then, the distribution medium was placed on the plate. Placed on top of it was an impermeable layer, into which a window approximately 1 in smaller than the preform had been cut on each side. The purpose of this window was only to avoid edge effects, and it was removed, together with the distribution medium, after the process was complete. A layer of release film was placed on top of these two layers so that they could be removed. The first seven layers of S2-glass were then placed on top of the release film so that the distribution medium would extend out from underneath the preform on one side. Then the separation layer was placed on top of the fiber preform. Generally, the polysulfone film was sandwiched between the epoxy adhesive before the part was laid up. Once the separation layer was in place, seven layers of S2-glass were placed on top of the preform, followed by another layer of release ply and a layer of distribution medium. At this point, the lay-up was complete. Two inlet tubes were used. One was placed on top of the preform, and the second one on the part of the bottom distribution medium that extended out from underneath the preform. The vacuum tube was placed at the opposite end of the preforms. This whole assembly was then placed under a vacuum bag, sealed, and vacuum applied. The vacuum serves three purposes: (1) it compacts the fabric; (2) it removes the air, thus reducing the number of voids in the composite; and (3) it creates a pressure difference that drives the impregnation of the resin into the spaces between the fibers.

A number of baseline panels were manufactured and tested, and the results from all specimens were compared. Two single-resin baseline panels were manufactured: one with a vinyl-ester matrix and the other with a phenolic matrix. The main purpose of these baselines was to assess the performance of the co-injected parts. The co-injected specimens would not be expected to perform better than the weaker of the two constituent materials. Finally, a panel was manufactured in a three-step process to simulate the current multistep procedure used to manufacture multilayer structures. Two panels were manufactured, one using phenolic resin and the other using vinyl-ester resin. Then, they were bonded together using the same adhesive film used in co-injection. To limit the number of variables, the polysulfone film was used together with the adhesive in an effort to compare manufacturing techniques.

**2.3 Materials.** One of the primary challenges presented by co-injection is the selection of a cure cycle. During co-injection, two or more polymers co-cure together; therefore, a cure cycle that allows the successful cure of all polymers must be selected. Since this application of CIRT<sup>TM</sup> is designed for large structures, the goal in selecting the materials was to maintain the cure cycle below 200°F (95°C). The vinyl ester used was Dow Derakane 411-350, which cures at room temperature using 0.2% by weight of cobalt naphthenate as the accelerator and 2% by weight of Trigonox 239A (organic peroxide) as the initiator. The phenolic was BP's J2027/L, a low-viscosity resole phenolic, which was catalyzed using 5% by weight Phencat 381. This phenolic must be cured at approximately 140°F in order to limit void formation due to the water present in the phenolic resin. Two adhesive films were selected for this study. The first was 3M's AF-163-2OST, which is an amine-cured epoxy-based adhesive. This adhesive is designed to cure at 225°F or higher. However, it has been shown that it is possible to cure it at temperatures as low as 200°F if the time periods are extended significantly. Another adhesive, a phenolic-epoxy (PH/EP), was selected due to better compatibility between the adhesive and the bulk phenolic. This resin is manufactured by Cytec-Fiberite as a film adhesive, HT 424. The compatibility is believed to be improved with this adhesive because PH/EP has a similar curing reaction to the bulk phenolic resin, whereas the epoxy adhesive has a much different curing reaction. As in the previous case, the PH/EP is designed to cure at elevated temperatures, 350°F, but, again, it is possible to lower the cure temperature by increasing the cure time.

The infusion of the part takes place at room temperature to facilitate the manufacturing process, particularly when this technology is used to manufacture large composite structures. After the infusion, the part is cured at 140°F (60°C) for 4 hr to cure the phenolic. It is necessary to go through this slow cure cycle to limit the formation of voids in the phenolic layer.

After the 4-hr cure of the phenolic, several variations of adhesive cure times were investigated. Two separate cases were investigated for the materials with 3M epoxy adhesive. The first was 4 hr at 200°F, which provided adequate cure when tested in the DSC. In addition, another set was cured at 200°F for an additional 24 hr. This time length was chosen as a maximum limiting time for the epoxy to co-cure with phenolic at 200°F. This cure cycle was investigated because there is a reaction between the acidic curing of the resole phenolic resin and the basic amine curing agent in the epoxy film adhesive. It was anticipated that this reaction could retard the cure of both resins in the interphase region. Therefore, an extended cure cycle was investigated to determine whether this retardation of the reaction could be compensated for by increased cure time. The goal of this new cycle schedule was to fully cure the adhesive while minimizing cure temperature for the manufacture of large structures.

The materials with the PH/EP film adhesive used the same 4-hr, 140°F cure cycle to cure the phenolic and were then cured for 4 hr at 200°F to cure the adhesive.

**2.4 SBS Testing.** SBS (ASTM 2344) is an extremely popular test due to its simplicity. This makes it a good tool to compare the shear strength and the overall quality of different composite specimens. Specimens were cut using a diamond-coated saw blade based on the dimensions dictated by the ASTM standard. Crosshead speed was set at 0.05 in/min (1.27 mm/min), and at least 10 specimens were tested for each type of specimen. The apparent shear strength was obtained using the following formula:

$$S_H = 0.75 \frac{P_B}{bd}, \quad (1)$$

where  $S_H$  is the apparent shear strength,  $P_B$  is the failure load,  $b$  is the width of the specimen, and  $d$  is the thickness. The majority of failures occurred at the interphase between dissimilar materials. Table 2 summarizes the results obtained. Results discussed in the text incorporate statistical variation (mean - 3 standard deviations [ $\sigma$ ]).

**Table 2. SBS Results**

Material	Apparent Shear Strength (psi)	Apparent Shear Strength Mean - 3 (psi)	Failure Type and Location
Vinyl Ester 411-350	5,360 $\pm$ 120	4,990	Brittle, midplane
Phenolic J2027/L	3,280 $\pm$ 120	2,930	Brittle, midplane
Multistep process	3,420 $\pm$ 230	2,720	Adhesive
Co-injected w/amine/epoxy adhesive (8-hr cure)	2,970 $\pm$ 70	2,760	Cohesive, phenolic side
Co-injected w/amine/epoxy adhesive (28-hr cure)	4,470 $\pm$ 100	4,170	Cohesive, phenolic side
Co-injected w/PH/EP adhesive (8-hr cure)	3,450 $\pm$ 80	3,210	1-in ply phenolic

The vinyl ester performed considerably better than all of the materials with shear strength of 5.0 ksi. The phenolic sample exhibited significantly lower shear strength (2.9 ksi) than the vinyl-ester baseline. The multistep and 8-hr-cure co-injection panels using the amine/epoxy adhesive (2.7–2.8 ksi) were slightly lower than the phenolic baseline. Notable improvements in shear strength are achieved with co-injected panels using the extended cure amine/epoxy adhesive (28 hr–4.2 ksi), as well as the PH/EP adhesive (8 hr–3.2 ksi). SBS tests show the potential for co-injected parts to provide equivalent or improved properties when cure cycles are optimized. Further research is required to fully optimize the process and performance.

**2.5 DCB Testing.** DCB measures Mode I fracture toughness, which is a measure of the resistance of the material to delamination within the interphase. The DCB test (ASTM D-5588) directly loads the interphase formed during processing. The DCB test is expected to be more sensitive to the performance of the various interphases created than the SBS test.



In the DCB specimen, an artificial flaw of known dimension was manufactured into the composite in the form of a precrack. The specimens were then cut from the composite panel. In this research, the specimens were approximately 24 mm wide and 300 mm long. Two blocks were then bonded to the end of the specimen where the precrack was located to allow loading of the specimen. One of the sides of the specimen was carefully painted, and evenly spaced marks were placed 5 mm apart. The crosshead speed was set at 0.5 mm/min. The specimens were placed in the fixture and the load was applied. As the load was applied, the crack tip propagated along the specimen. During the test, the critical load,  $P_{cr}$ , and the crosshead displacement,  $v_{cr}$ , were recorded at every crack-tip location.

These data were then used to obtain the fracture toughness of the material using the experimental compliance method, also known as Berry's method [14]. The benefit of this method is that it enables  $G_{Ic}$  vs.  $a$  to be determined and, consequently, the R-curve effects to be quantified through the following relationship:

$$G_{Ic} = \frac{nP_{cr}v_{cr}}{2Wa}, \quad (2)$$

where the critical load and the crosshead displacement are measured during the test,  $n$  is the power-law index relating compliance to crack length and fit to the data based on the following:

$$C = Ka^n. \quad (3)$$

The results of the DCB tests are summarized in Table 3. The vinyl ester demonstrates the highest fracture toughness (980 J/m<sup>2</sup>), followed by the co-injection panel using the PH/EP adhesive (730 J/m<sup>2</sup>). The other two co-injection panels exhibit fracture toughness similar to the phenolic panel (530–560 J/m<sup>2</sup>). The multistep process exhibited significant scatter in the results and yielded the lowest performance at 360 J/m<sup>2</sup>. All of the co-injected specimens showed cohesive failure. Note that the samples that used a PH/EP adhesive had the highest fracture toughness of any multiple resin material tested. The high Mode I fracture toughness of this material is most likely due to the chemical compatibility between the film adhesive and the

**Table 3. Summary of DCB Results**

<b>Material</b>	<b>Fracture Toughness (J/m<sup>2</sup>)</b>	<b>Fracture Toughness Mean - 3σ (J/m<sup>2</sup>)</b>	<b>Comments</b>
Vinyl ester 411-350	1,220 ± 80	980	Mostly brittle fracture at surface
Phenolic J2027/L	730 ± 60	550	SEM shows high void content
Multistep process	720 ± 120	360	failure at adhesive/phenolic interface
Co-injection (amine, 8-hr cure)	860 ± 100	560	failure in the adhesive, on the phenolic side; ductile behavior suggests material is not fully cured
Co-injection (amine, 28-hr cure)	740 ± 70	530	Cohesive failure in epoxy, on phenolic side, cracks also developed in first ply of phenolic
Co-injection (PH/EP 8-hr cure)	940 ± 70	730	Cohesive failure PH/EP adhesive

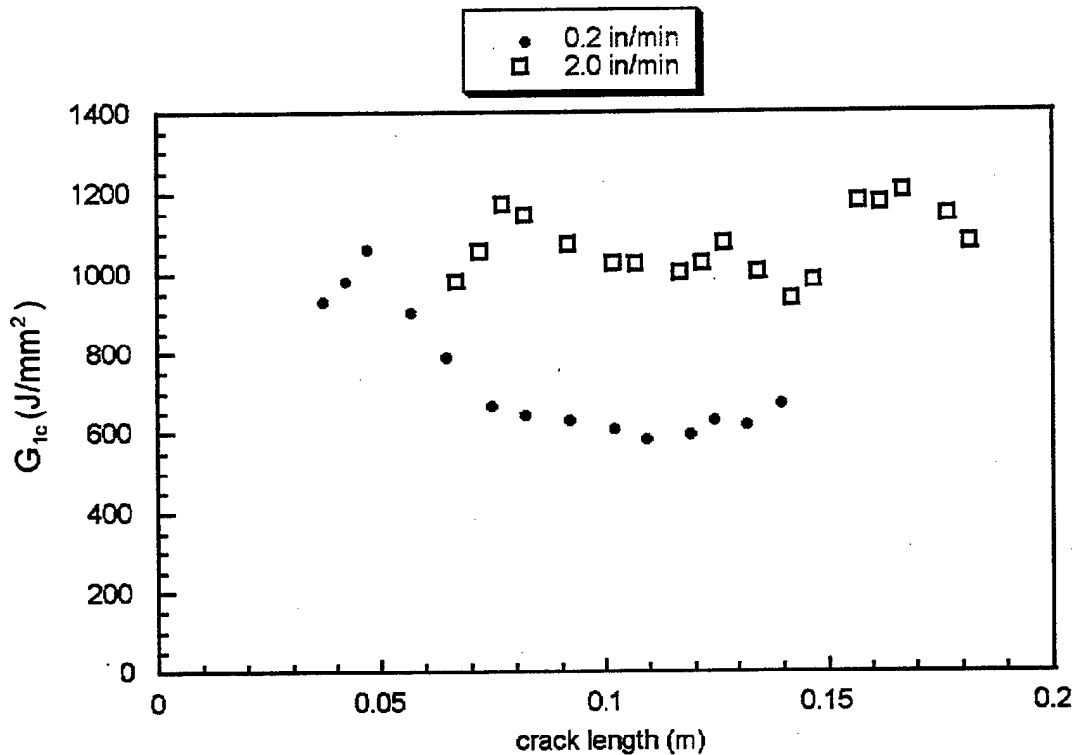
phenolic resin. Additionally, the precrack was placed both between the phenolic and the epoxy and between the epoxy and the vinyl ester, but this did not appear to affect the results. In most of the DCB samples, the failure was between the epoxy adhesive and the phenolic. It should also be noted that the specimens manufactured through a multistep process exhibited undesirable adhesive failure.

The co-injected specimens that used an epoxy/amine adhesive and were cured for only 8 hr exhibit a unique behavior: the fracture toughness decreases with increasing crack length. Additionally, during the tests, it was noted that the failure that occurred in the epoxy adhesive was always extremely ductile, displaying a behavior indicating that the epoxy had not fully cured. This stimulated the development of the 24-hr cure cycle. Partially cured thermoset resins would be expected to exhibit this behavior. It is difficult to characterize the local effects on cure and viscoelastic behavior that evolves during processing and interphase formation. Consequently, the DCB tests were conducted at higher rates to substantiate the mechanism.

Smiley and Pipes [15], as well as Gillespie, Carlsson, and Smiley [16], have studied the rate effects in the DCB test. These effects can be quantified by defining a crack-opening displacement rate as the opening displacement rate at a small arbitrary distance,  $\varepsilon$ , from the crack tip. The crack-opening displacement rate,  $\dot{y}_{cr}$ , is a function of both the crosshead speed,  $\dot{v}$ , and the crack length,  $a$ . The expression they derive is as follows:

$$\dot{y}_{cr} = \frac{3\dot{v}\varepsilon^2}{2a^2}. \quad (4)$$

Taking this into account, specimens were retested at a rate 10 times the original crosshead speed (5 to 50 mm/min). Results are compared to the lower rate data and clearly show the rate effect on Mode I fracture toughness. The decreasing fracture toughness behavior is not present at the higher loading rate, as shown in Figure 7.



**Figure 7. Fracture Toughness vs. Crack Length for Co-Injected Specimens Tested at Different Crosshead Speeds.**

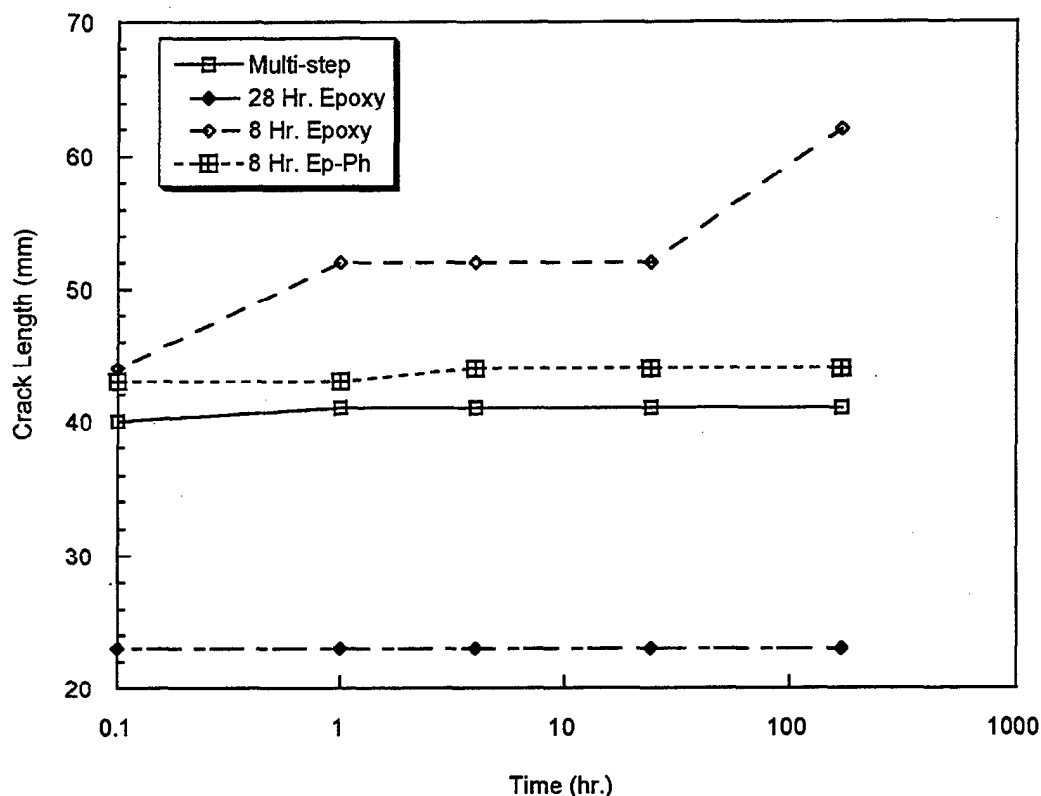
It is apparent from the behavior in these co-injected specimens that the epoxy adhesive did not fully cure. The joint exhibited rate-dependent behavior in both the DCB and in subsequent durability tests. This finding confirms that, in co-injection, it is not sufficient to define the cure cycle of the final part by simply combining the cure cycles of the individual materials.

Additional proof of the fact that the viscoelastic behavior is caused by a partially cured interphase is that the extended-cure-cycle (28 hr) specimens did not exhibit any kind of viscoelastic behavior. These specimens had a slight reduction of Mode I fracture toughness compared to the 8-hr-cure specimens. The fracture toughness remained constant or increased with increasing crack length, exhibiting a traditional R-curve behavior.

**2.6 Durability Tests.** The wedge test (ASTM D3762) was used to evaluate the performance of the interphase under adverse environmental conditions. The wedge test is performed on the same type of specimens used for the DCB. A wedge is inserted into the precrack to initiate a crack. The entire specimen is then inserted in water to simulate an adverse environment, and the crack propagation is recorded at regular time intervals. In this test, the highly stressed crack tip is continuously exposed to room-temperature water; therefore, its long-term durability can be evaluated. Figure 8 shows a graph of crack propagation vs. time for all phenolic/vinyl-ester hybrid samples. Under initial wedge insertion, cracks propagate and arrest to the distance at time,  $t = 0$ , as in Figure 8. The cracks are then measured at given time intervals over a testing period of 2 weeks. The crack in the co-injected specimen that uses the epoxy/amine adhesive and the short cure cycle, on the other hand, keeps propagating for longer times, exhibiting reduced durability. This is consistent with the viscoelastic behavior observed in the DCB tests. All other materials demonstrate superior durability in this environment.

### **3. Flammability Testing of CIRTM-Processed Vinyl-Ester/Phenolic Components**

**3.1 Introduction.** Phenolic-matrix composites have two advantages over other forms of fire protection: (1) the material contributes to the stiffness and strength of the composite material



*Note: The crack length at  $t = 0$  is the crack length after initial wedge insertion. Note that two cracks developed in the 28-hr specimens; only the interface crack length was reported.*

**Figure 8. Crack Length vs. Time for All Materials Tested.**

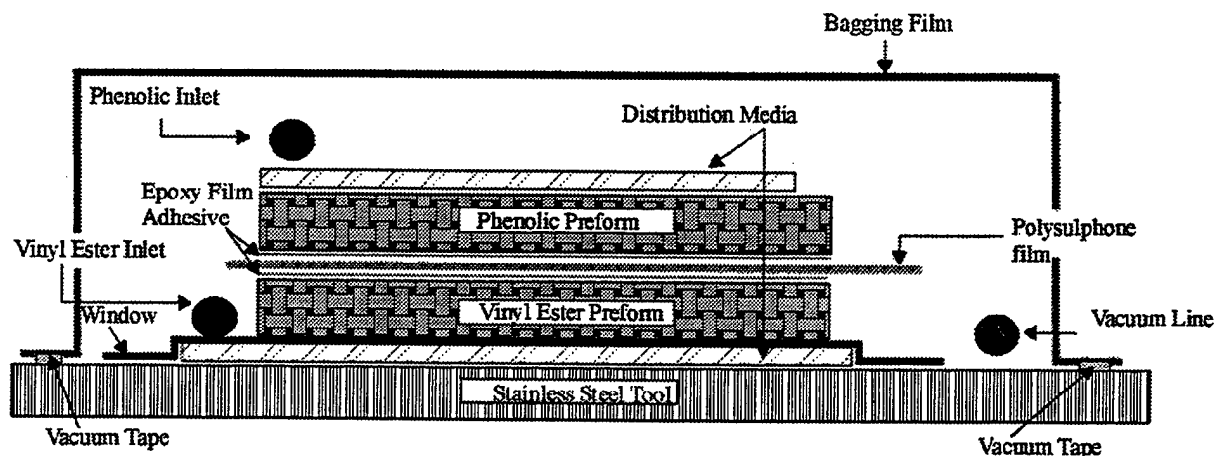
and may be incorporated into the design of the structure and (2) the cost of the phenolic resin is essentially equal to that of vinyl ester. This makes phenolic composites an attractive material from a cost standpoint vs. other costly fire protection such as intumescent paints and mats, as well as ablative materials.

The cone calorimeter is widely used to assess the flammability properties of materials on a small scale [17, 18]. It is a powerful tool for combustion analysis because it can monitor transient-heat-release rate (HRR), smoke production, and combustion gas evolution ( $\text{CO}_2$ ,  $\text{CO}$ ).

Organic-matrix composites have been studied previously using the cone calorimeter with and without incorporated fire barriers [19–24]. These studies demonstrate that the effective

combustion properties of composite materials are dependent not only on the matrix material, but also on the fiber type, volume fraction, and architecture. In addition, it has been shown that a fire-barrier material can provide vastly improved FST properties to composite materials with varying amounts of damage to the structural performance of the composite after exposure [21]. In this study, the cone calorimeter is used to ascertain HRR, smoke production, and time to ignition (TTI) properties of a variety of co-injected multilayer materials made of a vinyl-ester matrix composite structural layer and a phenolic-matrix fire-barrier layer. The results may be used to predict some of the full-scale FST trends for specific materials.

**3.2 Processing.** The lay-up for this study is shown in Figure 9. The materials selected were chosen for end-use properties, as well as processing performance. The vinyl ester chosen was the Dow Derakane 411-350 cured with an organic peroxide catalyst and cobalt-napthenate accelerator. The fire-retardant vinyl ester selected was the Dow Derakane 510A, also cured with organic peroxide and cobalt napthenate. The phenolic resin was the BP J2027 resole phenolic resin. The curing agent for this resin is BP Phencat 381 acid-based delayed-action catalyst. Two different thickness materials were studied in this work. The first was a 19-mm thick-section material and the second was a 6.5-mm thin laminate typical of GRP sandwich structures.



**Figure 9. The CIRTM Process for Vinyl-Ester/Phenolic Hybrid Composites.**

Three reinforcements were studied in the phenolic layer. First, an E-glass continuous strand mat (CSM), which produced a relatively low fiber-volume fraction of 0.25, was used. Second, a  $2 \times 2$  weave S-glass woven roving (WR) ( $0.64 \text{ kg/m}^2$ ), which gives a fiber-volume fraction of 0.50–0.55, was used. This was used instead of the E-glass WR used in the vinyl-ester layer, because the multipurpose sizing of the E-glass WR was not compatible with the phenolic resin, whereas the S-glass had a more compatible urethane sizing. The last reinforcement was the same S-glass WR stitched through the thickness with Kevlar thread on a 1-in square grid and a stitch density of 2 stitches/cm. The intent of the stitching was to determine whether through-thickness reinforcement could lessen the delaminations in the WR laminates. The thickness of each of the phenolic layers was 6 mm. This gave a total thickness of 19 mm for the thick-section hybrid composites. The thin-section materials were all composed of 10 plies of S2-glass WR. The CIRTM materials were composed of 5 plies each for the vinyl-ester and phenolic sections.

The interface layer used for all CIRTM materials in this study was composed of a 0.0254-mm-thick polysulfone (PSU) film sandwiched by 0.127-mm-thick epoxy film adhesive. This layer is designed to provide superior adhesion of the two layers through the use of DEA [25].

The cure cycle used for these specimens consisted of two stages. After injection, the vinyl ester was allowed to gel at room temperature for 30 min. The part was then heated for 4 hr at  $60^\circ\text{C}$  to cure the phenolic layer. Next, the part was vacuum-bagged again over the existing bag to provide compaction pressure during the cure of the adhesive. The temperature was then raised to  $120^\circ\text{C}$  for an additional 4 hr to cure the film adhesive and postbake the phenolic and vinyl-ester resins. The panels were then cooled, debagged, and cut into specimens for cone calorimeter testing.

**3.3 Testing.** All flammability testing was performed with the cone calorimeter using procedures outlined in ASTM D-1354. All materials were tested at an incident heat flux of  $50 \text{ kW/m}^2$  in duplicate. An initial round of testing determined that the multilayer specimens could not be tested reliably using the standard specimen size and edge frame. The reason for this

decision is that the edges and back side of the vinyl-ester section would ignite and combust and dominate the test results. This edge behavior is not representative of the large-scale material response and thus could not be used to predict the response of an actual structure. A modified specimen setup was devised using a larger specimen with an equal-size exposure area.

The actual specimen is  $150 \times 150$  mm in size and is inset into a fiberglass fireboard about 5 mm. The fireboard measures 200 mm square total and has a 100-mm-square cutout placed in the center to define the exposure area of the specimen. The edges of the specimen are sealed to the fireboard with high-temperature silicone sealant to attempt to draw vinyl-ester offgasses around the fireboard and away from the actual exposure area. This setup was successful and minimized edge behavior from affecting the results of the testing.

The test matrix is given as Table 4. The thick-section 19-mm CIRTM materials were tested only with 411-350 vinyl ester as the structural material. In the thin (6.5 mm) laminates, both the 411-350 and 510A vinyl esters were tested. In the thick-section laminates, the phenolic reinforcement was varied to study its effects, while, in the thin laminates, only WR reinforcement was used. The baseline materials were tested in the traditional specimen size and configuration. The phenolic materials were tested using a metal-edge frame and retaining grid due to the explosive delamination tendencies demonstrated by this material. The CIRTM processed hybrid materials were tested using the modified specimen setup described previously and were tested for a period of 30 min. After this time, the edge effects began to influence the test. This also allowed a visual comparison of damage in the panels after testing by means of sectioning the panels. All tests recorded TTI, HRR, and specific extinction area (SEA), as well as  $\text{CO}_2$  and CO levels.

**3.4 Results.** Average combustion parameters for the baseline and multi-layer materials are listed in Table 5. The values listed are averages of the two tests performed for each material. The TTI of the hybrid materials shows a large increase over the 411-350 vinyl ester and the 510A brominated vinyl ester. The brominated vinyl ester actually ignited more quickly than the standard vinyl ester, most likely due to the tendency of the fire-retardant vinyl ester to char quickly and then become less combustive. The 19-mm-thick J2027 phenolic/WR materials did



**Table 4. Test Matrix for Cone Calorimeter Testing**

Material No.	Vinyl-Ester Structural Layer	Phenolic Fire Barrier Layer	Processing	Thickness (mm)
1	Dow 411-350/WR	None	VARTM	19
2	Dow 510A/WR	None	VARTM	19
3	—	BP J2027/WR	VARTM	19
4	Dow 411-350/WR	BP J2027/CSM	CIRTM	19
5	Dow 411-350/WR	BP J2027/WR – stitched	CIRTM	19
6	Dow 411-350/WR	BP J2027/WR	CIRTM	19
7	Dow 411-350/WR	None	VARTM	6.5
8	Dow 510A/WR	None	VARTM	6.5
9	—	BP J2027/WR	VARTM	6.5
10	Dow 411-350/WR	BP J2027/WR	CIRTM	6.5
11	Dow 510A/WR	BP J2027/WR	CIRTM	6.5

**Table 5. Summary of Cone Calorimetry Data at 50 kW/m<sup>2</sup>**

Material No.	Structural Material	Thickness (mm)	Barrier Material	T <sub>ig</sub> (s)	300 s after ignition			Total Heat Released (kW/m <sup>2</sup> )	Average Heat Released (kW/m <sup>2</sup> )	Mass Loss (%)	Average SEA (m <sup>2</sup> /kg)
					Peak HRR (kW/m <sup>2</sup> )	Time (s)	Average HRR (kW/m <sup>2</sup> )				
1	411-350	19	None	79	221	22	135	209	86	18	1012
2	510A	19	None	62	130	24	100	217	76.0	29	483
3	J2027	19	None	DNI (30min)	—	—	—	—	—	—	—
4	411-350	19	CSM	326.5	100	29.5	66.8	368	86	18	226
5	411-350	19	WRST	416.5	62	277	48	28	81	6	460
6	411-350	19	WR	571	26	127	22	138	46	12	283
7	411-350	6.5	None	72	272	21	221	75	176	18	472
8	510A	6.5	None	67	126	15	90	38	86	30	380
9	J2027	6.5	None	762	31.1	139	27.7	18	24.5	18.8	122
10	411-350	6.5	WR	310	198	233	125	86.7	124	18	472
11	510A	6.5	WR	404	61	300	37	45	34.6	22	228

Note: SEA = Specific extinction area.

not ignite within 30 min at this heat flux. The specimens did delaminate explosively in a regular pattern, however. The highest TTI of the hybrid materials was the J2027/WR fire barrier, followed by the J2027/WR-ST. The TTI in the hybrid specimens appeared to be controlled by the permeability of the charred phenolic preform to the gasses given off by the vinyl ester during heating. This was a reason for the lower TTI in the stitched WR material. Although the fiber density is actually higher, the hole in the preform from the stitching provided a pathway for the vinyl-ester offgas and flames could be seen to emerge from along the lines of stitching. This permeability effect also accounted for the lower TTI times in the thin-section materials.

The HRR is an extremely important parameter in determining the potential threat of a material involved in a fire situation. The brominated vinyl ester, 510A, provides a much lower HRR 411-350 vinyl ester in both thick and thin sections. The thick-section CIRTM materials all demonstrate much lower HRR peaks and averages during the critical first 5 min, as well as over the entire test, compared to the 510A material. The best CIRTM material was with the J2027/WR fire barrier. This material had peak and average values of 26 and 22 kW/m<sup>2</sup>, respectively, at 300 s after ignition. This material did demonstrate explosive delamination in the phenolic layer during testing. The J2027/WR-stitched material did not delaminate during testing, probably due to the relief of water vapor pressure through the stitching holes in the preform. The HRR rate, however, was much higher than WR material alone, again due to the decrease in permeability due to the stitching. Finally, the J2027/CSM material showed the poorest performance among the hybrid materials due to the high permeability of the phenolic preform after the phenolic had burned and charred away.

In the thin-section materials, the 510A/J2027 material demonstrated performance approaching the phenolic baseline in both peak and average 300-s HRR. The 411-350/J2027 material substantially outperformed the 411-350 baseline but did not best the 510A material. This may be due to the decreased thickness of the phenolic layer. Thickness effects in composite materials can cause a dramatic change in the heat release properties due to the presence of the fiber after the resin has burned away. In this thickness material, the use of fire-retardant vinyl esters is recommended for superior flammability performance.

The smoke production properties of the CIRT<sup>TM</sup> processed hybrid composites as judged by the SEA are also improved over the fire-retardant vinyl ester. These values follow the HRR rate in general and are the lowest in the J2027/WR phenolic layer material.

**3.5 Conclusions.** The results of this testing have proven that CIRT<sup>TM</sup> manufactured hybrid materials can provide greatly improved properties over those of fire-retardant vinyl-ester matrix materials. In addition, results here have demonstrated that a non-fire-retardant vinyl ester may be used in thick-section laminates in conjunction with a WR/phenolic fire barrier and still yield outstanding flammability performance. This material would provide some cost savings over using a fire-retardant vinyl ester. In thin-section multilayer laminates, the fire-retardant vinyl ester provides far superior performance as compared to the non-fire-retardant vinyl ester. Here, the additional cost of a fire-retardant vinyl ester is justified.

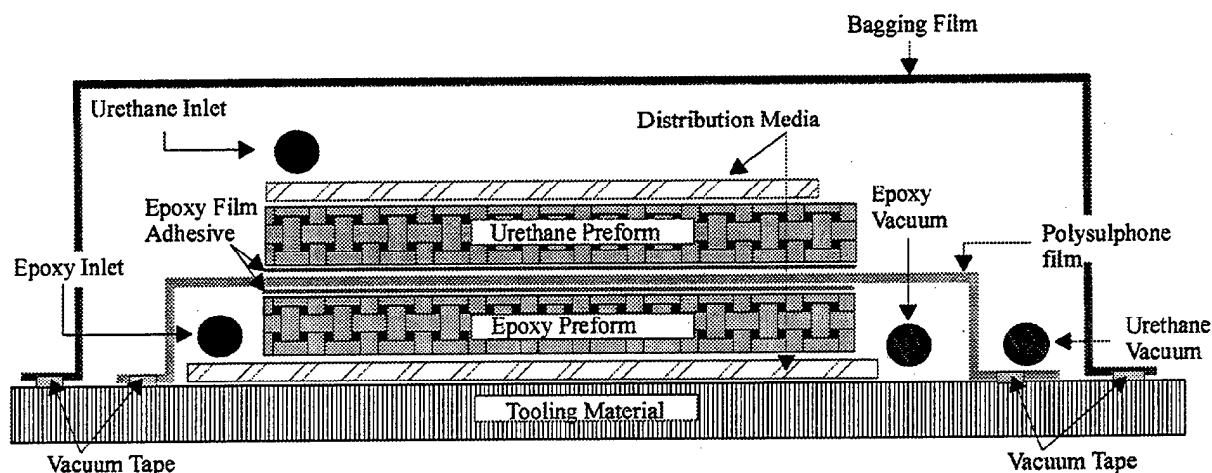
## **4. Processing and Impact Testing of Multilayer Polyurethane/Epoxy Composites**

**4.1 Introduction.** Low-velocity impact of composite materials has been studied extensively due to the high loss in structural properties after an impact with little or no visual damage. Many techniques have been investigated to improve the impact toughness of advanced composite materials including matrix, fiber, and interface modifications [26]. The effects of matrix materials and these are discussed in detail in this section. Many alterations to matrix materials have been made to improve the impact resistance of composite materials, including toughened thermoset resin systems and thermoplastic matrices [27, 28] and the combined use of both of these in a hybrid matrix composite [29]. These techniques have demonstrated some success in decreasing the size of damage area and increasing the residual compressive strength of the materials at the expense of reduced structural properties in the undamaged state. Masters and Evans [28] have conducted a study that shows there is a high correlation between Mode II (forward shear) fracture toughness and compression-after-impact (CAI) properties. At low-impact velocities in brittle matrix composites, the dominant visual damage mechanism is generally interlaminar failure (delamination), which initiates and propagates due to stress wave

propagation and flexural vibrations. Polyurethane's offer the potential to attenuate stress wave amplitude during impact loading, as well as absorb significant amounts of energy due to their high fracture toughness.

This section addresses the manufacture and performance of a multifunctional hybrid composite material produced with CIRTM processing composed of a carbon-fiber/epoxy structural layer and a carbon-fiber/polyurethane protective layer. Polyurethane-matrix composites possess outstanding vibration-damping and wear-resistance properties. Very little information has been published concerning the effects of multiple matrix materials on low-velocity impact properties. One study performed has investigated the use of hybrid matrix composites [5]. Here, the impact and energy absorption performance of materials with alternating thermoplastic and thermoset layers was studied. The authors concluded that the semi-crystalline thermoplastic matrix materials had fundamentally higher energy absorption attributes than the brittle epoxy layers due largely to the lower fiber-matrix bonding strength. However, these properties were not evidenced in the hybrid composites because of the poor interfacial toughness between the thermoplastic and thermoset layers. Delaminations between these two layers accounted for much of the energy absorbed in these systems, which led to low residual flexural strength.

**4.2 Processing.** Figure 10 shows the lay-up used for this study. The epoxy resin used was an anhydride-cured standard bis-phenol A-type epoxy system produced by Ciba-Geigy (GY 6010-HY 917). The polyurethane resin used was a thermoset polyurethane manufactured by Uniroyal (Adiprene L100) and cured with a temperature-blocked amine curing agent (Caytur 21), also from Uniroyal. To isolate the effects of the urethane matrix material, only one reinforcement type was used for both layers of the composite. This was a WR fabric, 8-k tow, AS4 carbon fiber, in a five-harness satin weave. The resin flow separation was maintained through the use of a 0.127-mm-thick PSU film. Epoxy film adhesive was placed on each side of the PSU film to provide good adhesion between the film and structural layers. This adhesive was an amine-cured type and was designed to exploit the DEA mechanism, where epoxy and



**Figure 10. VARTM Setup Used for Co-Infusing Epoxy and Urethane Resins Simultaneously.**

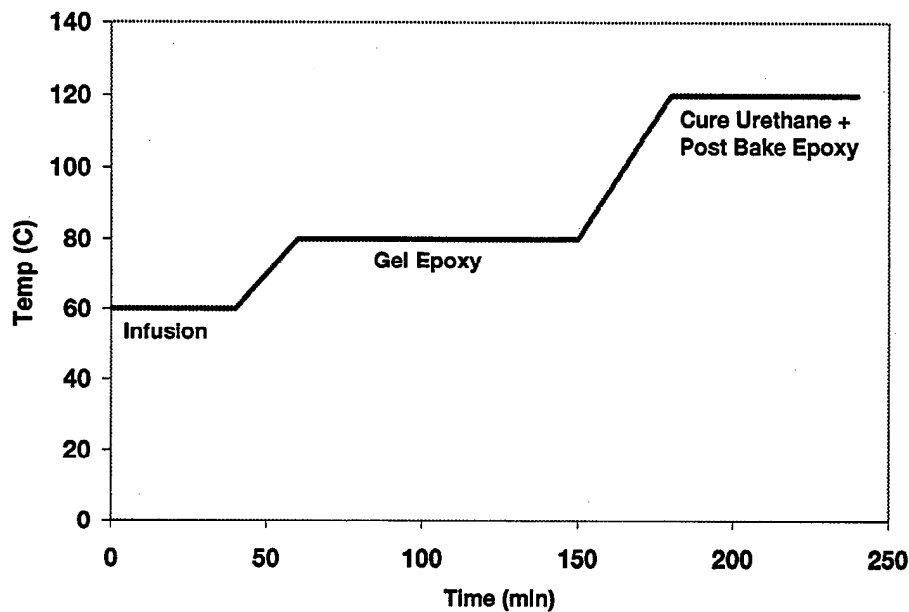
amine diffuse into the thermoplastic layer and react to form a strong interpenetrating network between the thermoplastic and thermoset materials [25].

Much of the challenge in processing epoxy and urethane hybrid composites is the necessity of elevated-temperature injection and cure of the resins. The cure and viscosity information for the epoxy and urethane resins is summarized in Table 6. At elevated temperatures, the viscosity difference between the urethane and epoxy resins becomes extreme. The urethane has a tremendously high viscosity ( $>2,000$  cps) and that of the epoxy resin is very low ( $\approx 50$  cps). Due to this dissimilarity, it was necessary to isolate each of the individual resins.

The temperature profile for the processing of urethane and epoxy simultaneously is shown in Figure 11. The schedule is a compromise between the optimum cure schedules for each of the two resins. Due to the high room-temperature viscosity of the urethane resin, the infusion must be performed at  $60^{\circ}\text{C}$ . This temperature was chosen as an optimal combination of the resin pot life and viscosity. Each of the resin components was preheated prior to infusion. Just before infusion, the resins were mixed and degassed, and then placed into the oven and connected to the injection lines. The infusion times of a typical  $50 \times 60$ -cm panel made were 30-60 min and were dependent on the thickness of the urethane layer. The urethane resin infusion through the

**Table 6. Individual Processing Details for the Epoxy and Polyurethane Resins**

Resin	Curing Agent	Injection Temperature (°C)	Gel Temperature (°C)	Post Bake Temperature (°C)
Ciba-Geigy 6010 epoxy	Ciba-Geigy HY 917 anhydride	30	80	120
Uniroyal L100 polyurethane	Caytur 21, blocked amine catalyst	60	120	120



**Figure 11. Processing Temperatures for CIRTM Processing of Epoxy and Urethane.**

thickness was determined with a flow and cure sensor monitoring system developed by the U.S. Army Research Laboratory (ARL) and the University of Delaware Center for Composite Materials [30, 31]. The epoxy infused in 4–5 min. After the urethane was completely infused, the temperature was raised to the recommended epoxy gel temperature of 80° C. At this temperature, the viscosity of the epoxy resin becomes extremely low and the vacuum pressure starts to pull large amounts of resin through the part. Once the resin gels in the supply tube, this effect will start to remove resin from the preform, resulting in a large void content within the part. To counter this effect, the vacuum pressure on the epoxy side only was decreased to

4-5 mmHg, where very little epoxy was drawn from the part but was still not allowed to drain into the part.

The control specimens made entirely of epoxy or urethane were manufactured using similar VARTM processing. Here, the manufacturer's recommended processing temperatures were observed.

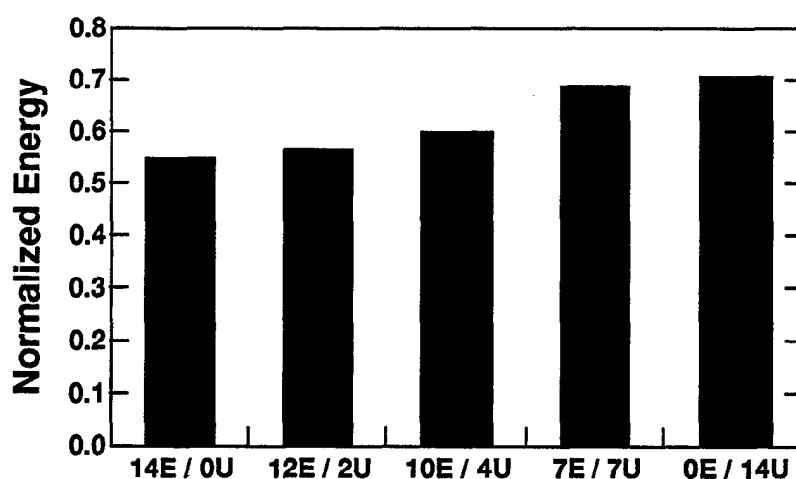
Impact specimens were machined from panels manufactured using the aforementioned outlined techniques of approximate dimensions  $50 \times 60$  cm. Each of the specimens was cut from these panels to dimensions of  $100 \times 150$  mm. Exact construction details of the specimens are provided in Table 7. The panels were fabricated to have an approximate thickness of 6.5 mm, which required the use of a total of 14 plies of fabric in each preform.

**Table 7. Specimen Identification and Construction Details**

Material Name	Number of Epoxy Plies	Number of Urethane Plies	Epoxy (%)	Urethane (%)
14 E/0 U	14	0	100	0
12 E/2 U	12	2	86	14
10 E/4 U	10	4	71	29
7 E/7 U	7	7	50	50
0 E/14 U	0	14	0	100

**4.3 Impact Testing.** The impact testing was done using a standard instrumented drop tower apparatus and a hemispherical impact tup 15.9 mm in diameter. The specimens were each impacted with 6.67-J/mm (1,500 in-lb/in) energy with a constant mass including the impactor of 10.98 kg. The initial impact velocity of the tup for all specimens was 2.8 m/s. The specimen is supported over an impact area of dimensions  $75 \times 125$  mm and is held in place by four point-type spring clamps. The impactor was caught after the initial impact to prevent multiple impacts. Data from the load cell was collected from a microcomputer-based data-acquisition system at a rate of 400 kHz. The data were used to calculate the tup energy, velocity, deflection, and acceleration from kinematics relationships.

**4.4 Results and Discussion.** Data collected from the impact event for each of the five materials studied indicate that the highest load values are in the 100% epoxy specimens and the lowest in the 100% urethane specimens. Each of the other three fractional panels falls in between these extremes. It was also noted that the total time of the impact event becomes increasingly longer for higher percentages of urethane in the specimen. The energy curves also indicated that the peak energy is constant, as would be expected, but the final energy increases for larger fractions of urethane in the specimen. This effect was calculated for all impacted specimens and is presented in Figure 12 as the normalized energy absorbed for each specimen. There is a noticeable trend for higher energy absorption as the urethane content of the material is increased. Examining the deflection curves, one can see that the deflection of the 100% urethane specimen is more than twice that of the epoxy baseline. The fractional samples have deflections somewhere in between, although it is interesting to note that there is a large jump between the 7-ply epoxy/7-ply urethane and the 10-ply epoxy/4-ply urethane.



**Figure 12. Normalized Energy Absorbed.**



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6. AUTHOR(S)  Bruce K. Fink, John W. Gillespie Jr.*				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  U.S. Army Research Laboratory ATTN: AMSRL-WM-MB Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER  ARL-TR-2125	
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13. ABSTRACT (Maximum 200 words) <p>Vacuum-assisted resin transfer molding (VARTM) processes have been proven to be cost-effective manufacturing techniques for large composite structures. However, their use has been limited to single resin systems. A large variety of composite structures requires multiple resins to serve different purposes while being integrated into a single structure. Significant environmental cost savings are possible by replacing currently practiced sequential repair and manufacturing techniques with reduced-step co-cure processes enabled by the co-injection resin transfer molding (CIRTM) variant of the VARTM process. The CIRTM process was investigated to manufacture two dual-layered structures commonly required in Department of Defense (DOD) structures. The first consists of a vinyl-ester layer for structural integrity and a phenolic layer for flammability, smoke, and toxicity (FST) protection. The second consists of structural epoxy with a polyurethane layer for improved damage tolerance. In each case, the two resins are simultaneously injected into a mold filled with a stationary fiber bed and co-cured. Resin separation is maintained by a 1-mil-thick polysulfone film sandwiched between two layers of 6.5-mil-thick adhesive. Various tests have been performed to demonstrate mechanical, thermal, and rate-dependent performance of the improved structures.</p>				
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